UTS UNIVERSITY OF TECHNOLOGY SYDNEY

Influence of Cement Composition and Curing Regimes on the Susceptibility of Heat-Cured Cementitious Systems to Delayed Ettringite Formation

by

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under the supervision of

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Certificate of Original Authorship

I, *Yogesh Kumar Ramu* declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy in the School of Civil and Environmental Engineering, Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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Date: June 26, 2020

This thesis is dedicated to my family

"Though things diverse from divers sages' lips we learn,
'Tis wisdom's part in each the true thing to discern "
Thiruvalluvar

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Abstract

Delayed ettringite formation (DEF) occurs in precast concrete elements and mass concrete structures where curing temperature and/or high heat of hydration delays the formation of ettringite; which instead forms at the later stage of hydration. The late crystallisation of ettringite may cause localised cracks, as it occurs within the confined spaces of the hardened concrete matrix. The presence of such cracks may reduce the service life of the structure. Previous research indicates that curing concrete above 70°C, cement sulphate, alkali, and aluminate content as vital factors contributing to deleterious DEF. However, linking deterioration of concrete with a mere presence of DEF needs further investigation.

In this research, two Australian general-purpose cements with different alumina contents have been used to prepare a matrix of cementitious systems with varying sulphate and alkali levels. The effect of different heat curing regimes on these cementitious systems had been investigated. Mortar prisms length and mass changes had been recorded for 600 days. Various characterisation techniques such as X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), pore solution analysis, scanning electron microscopy (SEM) image and elemental analysis were used to understand the phase development of hydration products, microstructure and ettringite deposition location. Electrochemical impedance spectroscopy (EIS) had been used to study implications of heat curing in microstructure and its relevance to DEF.

For systems using the as received GP cements, with no elevation of the sulphate and alkali contents, no expansion was observed in heat-cured mortars, although DEF was noted in TGA and XRD analysis of parallel cured cement pastes. Similar results were obtained for the sulphate or alkali modified cements. Significant expansion and mass gain, however,

was observed in cementitious systems containing 4% SO_3 and 1% Na_2O_{eq} when cured at 80-90°C for 8-12 hours. The XRD analysis of the parallel cured cement pastes reveal that the quantity of DEF was higher in expanding mortars than the non-expansive ones. Further, localised DEF was observed in the microstructure in the interfacial transition zone (ITZ). The resistivity for expanding mortars was observed to be significantly lower than the non-expanding mortars, indicating microstructural changes associated with the precipitation of DEF resulting in increased number conduction pathways.

The efficacy of fly ash (FA) in mitigating DEF was also tested by incorporating 25% FA in the mortar mixes which gave maximum expansion; mortars containing 4% SO_3 and 1% Na_2O_{eq}. Results demonstrated that FA was effective in mitigating expansive DEF.

The outcomes of this investigation suggest that precast concretes manufactured using Australian GP cements cured below 80°C are unlikely to be subject to DEF. Concrete mixes that contain GP cements and FA are even less likely to be subject to expansive DEF.

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List of Abbreviations

ACI	American Concrete Institute
AFm	calcium aluminate monosulphate phases (Al_2O_3-Fe_2O_3-mono)
AFt	calcium aluminate trisulphate phases (Al_2O_3-Fe_2O_3-tri)
AS	Australian Standards
ASR	alkali-silica Reaction
ASTM	American Society for Testing and Materials
ATIC- SP	Australian Technical Infrastructure Committee- standard procedure
BSE	back scattered electron
C-A-S-H	calcium-alumino-silicate-hydrate
CCFA	class C fly ash
CFFA	class F fly ash
CH	calcium hydroxide or portlandite
C-S-H	calcium-silicate-hydrate
DEF	delayed ettringite formation
EDS/EDX	energy-dispersive X-ray spectroscopy
EEF	early ettringite formation
EIS	electrochemical impedance spectroscopy
Et	ettringite
FA	fly ash
FTIR	Fourier transform infrared spectroscopy
Hc	hemicarbonate
Hg	hydrogarnet
ICP-OES	inductively coupled plasma - optical emission spectroscopy
IP	inner product (C-S-H)
IPA	isopropanol
ITZ	Interfacial Transition Zone
Mc	monocarbonate
Ms	monosulphate
NDT	Non-Destructive Testing
OP	outer product (C-S-H)

qXRD	quantitative X-Ray diffraction
Qz	quartz
RH	relative humidity
SEF	secondary ettringite formation
SEM	scanned electron microscopy
$(SO_3/Al_2O_3)_m$	cement molar ratio of SO_3 to Al_2O_3
TGA	thermogravimetric analysis
w/b	water to binder ratio by mass
w/c	water to cement ratio by mass
XRD	X-ray diffraction
XRF	X-ray fluorescence

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